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Optical Studies of a Layered Manganite $La_{1.2}Sr_{1.8}Mn_2O_7$: Polaron Correlation Effect

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Optical conductivity spectra of a cleaved *ab*-plane of a $La_{1.2}Sr_{1.8}Mn_2O_7$ single crystal exhibit a small polaron absorption band in the mid-infrared region at overall temperatures. With decreasing temperature (T) to Curie temperature (T_C), the center frequency of the small polaron band moves to a higher frequency, resulting in a gap-like feature, and that it collapses to a lower frequency below T_C. Interestingly, with decreasing T, the stretching phonon mode hardens above T_C and softens below T_C. These concurring changes of lattice and electronic structure indicate that short range polaron correlation exist above T_C but disappear with a magnetic ordering.

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Recent studies on manganites have shown that there exist strong coupling among spin, charge, orbital, and lattice degrees of freedom. The relative coupling strength of those degrees of freedom can be sensitively affected by variation of physical parameters, such as amounts of carrier doping, and/or structural modification. For example, the structure of cubic perovskite (La,Sr)MnO_3 can be modified into a layered one by inserting a rock-salt-type block layer $(La,Sr)_2O_2$ into every n-MnO_2 sheets, i.e., by forming the Ruddlesden-Popper compound, $(La,Sr)_{n+1}Mn_nO_{3n+1}$. With the variation of structures from single– (n=1: K_2NiF_4 structure), double– (n=2) and ∞– (cubic perovskite) MnO_2 sheet, physical properties of these materials are sensitively varying.[1] In addition, the effective low dimensionality of the reduced n system can enhance charge and spin fluctuations to induce more localized tendency than the cubic one.

$La_{1.2}Sr_{1.8}Mn_2O_7$, which has the double MnO_2 sheets, is a prototypical material that exibits intriguing interplays of various degrees of freedom. Although it becomes a ferromagnetic (FM) metal below Curie temperature (T_C) at 126 K, earlier studies showed significant local Jahn-Teller (J-T) lattice distortions at overall temperatures[2] and short range antiferromagnetic spin order.[3] A more recent study also provided a clear evidence of lattice polaron formation above T_C by showing diffuse X-ray scattering around the Bragg peaks. At the same time, the scattering experiments indicated an existence of short range polaron ordering by showing incommesurate satellite peaks.[4]

Optical spectra for this bilayered system have been reported already.[5] However, there are no systematic optical investigations how polaron effects with short range correlation become manifest in the optical spectra. In this report, we present detailed optical conductivity spectra which reveal interplays of spin, charge, and lattice degrees of freedom in $La_{1.2}Sr_{1.8}Mn_2O_7$. With decreasing T, the mid-infrared small polaron band moves to a higher frequency up to T_C and then becomes collapsed to a lower frequency below T_C. And, the stretching phonon mode hardens above T_C and softens below T_C. These concurring changes of lattice and electronic structure support the existence of the enhanced polaron (charge) correlation above T_C and its sudden collapse below T_C. A single crystal of $La_{1.2}Sr_{1.8}Mn_2O_7$ was grown by the floating-zone method using a mirror furnace. The sample was characterized by resistivity and magnetization measurements.[6] For optical reflectivity measurements, a

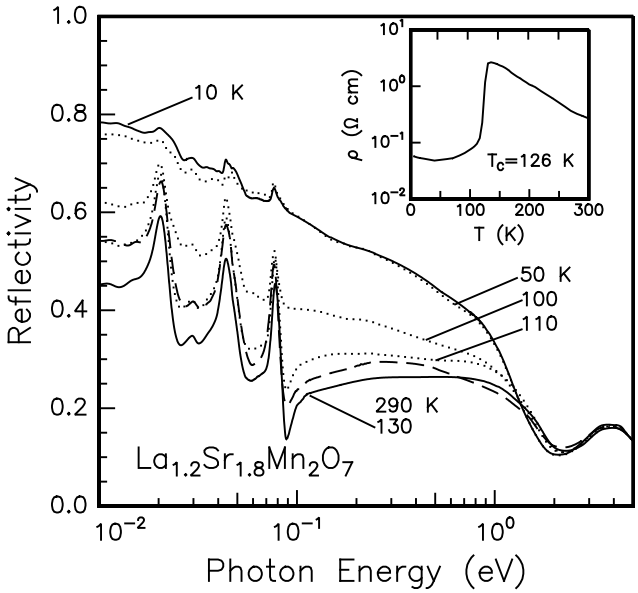

FIG. 1. T-dependent $R(\omega)$ of $E \parallel ab$ for the $La_{1.2}Sr_{1.8}Mn_2O_7$ single crystal. Inset: in-plane $\rho(T)$ with T_C=126 K.

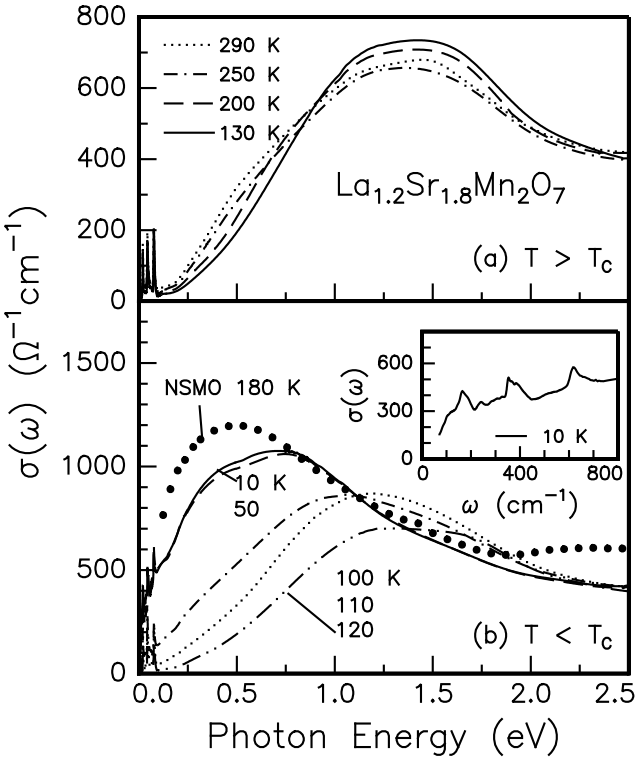

FIG. 2. (a) $\sigma(\omega)$ of $La_{1.2}Sr_{1.8}Mn_2O_7$ for $T > T_C$ and (b) $T < T_C$. The solid circles in (a) and (b) represent the $\sigma(\omega)$ of $Nd_{0.7}Sr_{0.3}MnO_3$ at 180 K. Inset of (b) : $\sigma(\omega)$ of $La_{1.2}Sr_{1.8}Mn_2O_7$ in the low frequency region at 10 K.

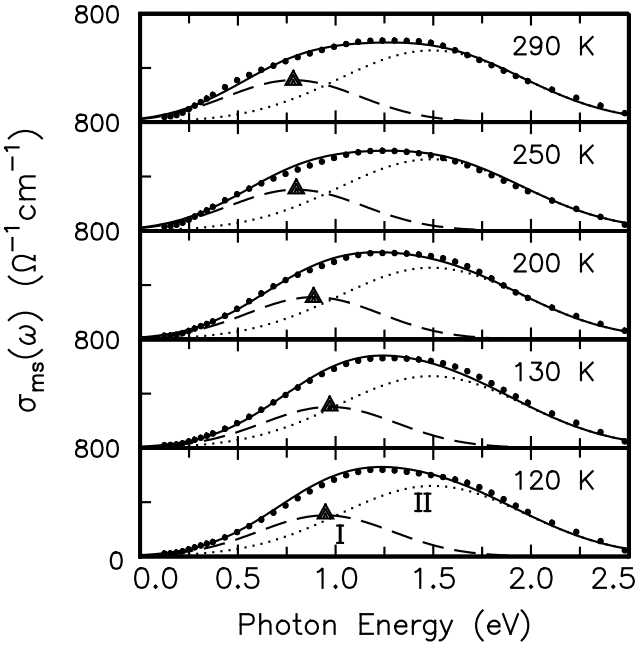

FIG. 3. $\sigma_{ms}(\omega)$ of $La_{1.2}Sr_{1.8}Mn_2O_7$. The solid circles are experimental data. The dotted lines represent fixed Gaussian functions around 1.5 eV (Peak II). The dashed lines show small polaron fitting using the Gaussian function (Peak I). The solid lines represent the sums of two Gaussian functions. The solid triangles represent the center of Peak I.

cleaved *ab*-plane was freshly prepared. Details for the reflectivity measurements were described in our previous report.[7] Using the Kramers-Kronig relation, we obtained optical conductivity spectra $\sigma(\omega)$ from reflectivity spectra $R(\omega)$.

Figure 1 shows T-dependent $R(\omega)$ of the cleaved *ab*-plane of $La_{1.2}Sr_{1.8}Mn_2O_7$. At 290 K, there are three sharp peaks originating from optic phonon modes in the far-infrared region. With T approaching T_C, $R(\omega)$ below 0.4 eV decrease, which is consistent with the dc resistivity behavior shown in the inset of Fig. 1. As T decreases further below T_C, $R(\omega)$ start to increase significantly, apporaching to a metallic response.

T-dependent $\sigma(\omega)$ both above and below T_C are displayed in Figs. 2 (a) and (b), respectively. Above T_C, $\sigma(\omega)$ show a broad absorption band around 1.2 eV. The shape of $\sigma(\omega)$ at 290 K looks similar to that at 250 K. However, as T approaches 130 K, $\sigma(\omega)$ below 0.5 eV become suppressed to show a finite gap-like feature. At the same time, the height of the broad band near 1.2 eV increases to form a sharper band. On the other hand, as T is lowered below T_C, the spectral weight moves suddenly to a lower energy region as shown in Fig. 2 (b). The shape becomes rather asymmetric and its magnitude below 1.0 eV increases significantly, indicating that a large spectral weight become transferred from a higher energy region with the onset of the magnetic ordering.

To get further insights, we compared the T-dependent $\sigma(\omega)$ of $La_{1.2}Sr_{1.8}Mn_2O_7$ with those of $Nd_{0.7}Sr_{0.3}MnO_3$ (NSMO),[7] which is a cubic perovskite with a similar metal-insulator transition. Compared with the other cubic perovskite manganites such as $La_{0.7}Ca_{0.3}MnO_3$[8] and $La_{0.7}Sr_{0.3}MnO_3$,[9] NSMO has a relatively low T_C around 200 K, due to a reduced electron bandwidth. It is now well established that small polaron plays an important role in the paramagnetic insulating regime of the perovskite manganites.[10] Furthermore, a recent X-ray and neutron scattering studies on $La_{1.2}Sr_{1.8}Mn_2O_7$ showed the existence of polarons in the paramagnetic state.[4] Therefore, it is quite reasonable that optical spectra of $La_{1.2}Sr_{1.8}Mn_2O_7$ above T_C can be analyzed by the polaron picture.[10]

There exist some differences in the spectra of $La_{1.2}Sr_{1.8}Mn_2O_7$ and NSMO. First, $\sigma(\omega)$ of NSMO and other cubic perovskites were reported to be nearly T-independent above T_C.[7–11] However, $\sigma(\omega)$ of $La_{1.2}Sr_{1.8}Mn_2O_7$ below 2 eV show a systematic T-dependence above T_C. As T approaches T_C, spectral weight below 1.0 eV decreases, but that above 1.0 eV increases. Second, $\sigma(\omega)$ of $La_{1.2}Sr_{1.8}Mn_2O_7$ do not show a Drude-like peak even at 10 K (see the inset of Fig. 2 (b)). In the FM metallic states of the cubic perovskite manganites,[7–11] the small polaron spectral weight was transferred to a lower energy to form an asymmetric mid-infrared band and a finite Drude-like peak at very low T,

which were interpreted as incoherent and coherent absorption bands of a large polaron, respectively. The lack of the Drude peak in the $\sigma(\omega)$ of $La_{1.2}Sr_{1.8}Mn_2O_7$ can be related to its effective low dimensionality, induced by a decrease of the number of the MnO_2 sheet (i.e. $n = 2$). Third, the lineshape of the $La_{1.2}Sr_{1.8}Mn_2O_7$ absorption band at 10 K ($\approx 0.1T_C$, $T_C = 126$ K) is quite similar to that of NSMO at 180 K ($\approx 0.9T_C$, $T_C = 198$ K), as shown in Fig. 2 (b). Note that $\sigma(\omega)$ of NSMO at 180 K is close to that of 200 K (above T_C) in its shape, without showing the Drude-like peak.[7] These observations indicate that $La_{1.2}Sr_{1.8}Mn_2O_7$ remain as the small polaron state even far below T_C. Therefore, it is reasonable that the $\sigma(\omega)$ of $La_{1.2}Sr_{1.8}Mn_2O_7$ can be analyzed in the small polaron picture at all temperatures.

To get a more quantitative information on the small polaron absorption, we analyzed the experimental $\sigma(\omega)$ in terms of $\sigma(\omega) = \sigma_{ms}(\omega) + \sigma_L(\omega)$.[12] Here, $\sigma_{ms}(\omega)$ represent the conductivity contribution of the two mid-gap states below 2.0 eV and $\sigma_L(\omega)$ correspond to the charge-transfer transition between O $2p$ and Mn e_g levels, centered around 4.0 eV. By fitting with a Lorentz oscillator, we determined $\sigma_L(\omega)$ and subtracted it from the experimental $\sigma(\omega)$ to obtain $\sigma_{ms}(\omega)$. For fitting $\sigma_{ms}(\omega)$, we used two Gaussian functions as shown in Fig. 3.[13] One is located below 1.0 eV (Peak I) and the other is around 1.5 eV (Peak II).[14,15] Peak I corresponds to the small polaron absorption related to a nearest neighbor hopping from Mn^{3+} to Mn^{4+},[7–11] and Peak II corresponds to on-site $d - d$ transition.[16] Interestingly, $\sigma_{ms}(\omega)$ above and just below T_C can be well described when only the center frequency of Peak I, ω_I, is assumed to be T -dependent, while the other parameters such as the strength and the width of Peak I are fixed. And, Peak II are nearly T -independent within 3 %. Fig. 3 shows the fitting results above and just below T_C. With lowering T further, the best fitting was obtained when the strength of Peak I as well as ω_I was assumed to change with a slight variation of the strength of Peak II.

Fig. 4 (a) shows T-dependence of ω_I obtained by the fitting process. As T becomes lower in the paramagnetic region, ω_I clearly increases from 0.8 to 1.0 eV. With magnetic ordering at T_C, ω_I starts to decrease abruptly to reach a finite value of 0.58 eV at 10 K. In case of an adiabatic small polaron, ω_I corresponds to two times of the small polaron binding energy.[17] Therefore, above results indicate that the coupling between charge and lattice should exist far above T_C and that its strength be enhanced near T_C. And, the coupling strength suddenly decreases to a lower value with the influence of spin ordering.

The increase of ω_I at the high T region is responsible for the apparent suppression of $\sigma(\omega)$ below 0.4 eV, shown in Fig. 2 (a). The suppression of the $\sigma(\omega)$ produces a finite gap-like tail below 0.4 eV. The tail moves systematically to a higher energy between 250 K and T_C and the gap-like behavior becomes evident around 130 K just above T_C. This behavior is reminiscent of a finite

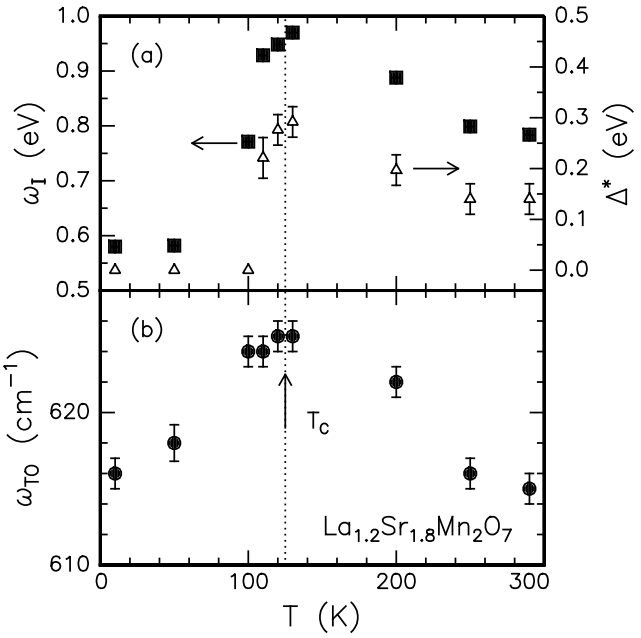

FIG. 4. (a) T-dependent center frequencies of Peak I (ω_I) and Δ^* [see the main text for definition] are represented by solid square and open triangle, respectively. Error bars in ω_I are smaller than the size of solid square. (b) The peak frequencies of the stretching phonon mode (ω_{TO}). The dotted line is a guide to depict T_C.

charge gap formation in the materials with a clear long range charge ordering (CO) at low T.[18,19] Because there is no evidence for the long range CO in $La_{1.2}Sr_{1.8}Mn_2O_7$, the peculiar behavior may suggest an existence of short range charge correlation above T_C. In reality, a recent scattering experiment confirmed the existence of this short range charge and polaron correlation that grows up near T_C and diminishs below T_C.[4] To quantify the short range charge order above T_C, we define Δ^* as a crossing point energy with the $\sigma(\omega) = 0$ line when a steeply increasing part of $\sigma(\omega)$ is linearly extrapolated. Fig. 4 (a) summarizes the T-dependent values of Δ^*. The T-dependence of Δ^* is quite similar to that of ω_I. With decreasing T to T_C, Δ^* gradually increases from 0.15 to 0.28 eV. The Δ^* suddenly starts to decrease at T_C and becomes zero below ~100 K. These experimental results of ω_I and Δ^* strongly support that polaron and charge correlations grow up to T_C and collapse due to the FM ordering.

The stretching optical phonon mode, related to the lattice degree of freedom, also reflects the existence of short range charge and polaron correlations above T_C. Figure 5 presents T-dependence of the phonon mode ω_{TO} located around 615 cm^{-1} at 290 K. With lowering T to T_C, ω_{TO} shows a significant hardening. When T is further lowered, the phonon mode softens. Figure 4 (b) shows the values of ω_{TO} determined by fitting with the Lorentz oscillator. Between 290 and 130 K, ω_{TO} increases by about 10 cm^{-1}. With lowering T, it is clearly shown

that $\omega_{\rm TO}$ decreases abruptly to 616 cm^{-1} at 10 K.

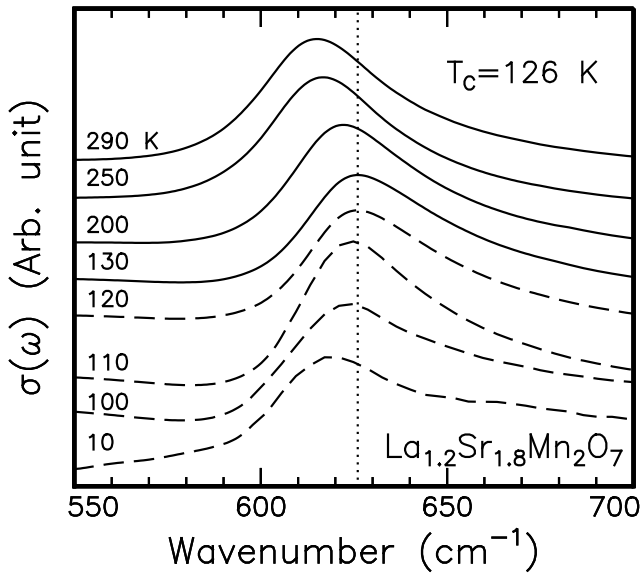

FIG. 5. T-dependence of the optical stretching phonon modes. The solid and the dashed lines are phonon modes above and below T_C, respectively. The dotted line represents the peak frequency of the phonon mode around 625 cm^{-1} at 130 K.

The frequency shift of the stretching mode reflects that there exist significant modulations of local Mn-O bond lengths.[20] In long range CO systems, the stretching phonon mode hardens near CO temperature, $T_{\rm CO}$: the observed frequency shifts were about 15 cm^{-1} and 25 cm^{-1} in case of $La_{0.5}Ca_{0.5}MnO_3$[21] and $Bi_{0.18}Ca_{0.82}MnO_3$,[19] respectively. The hardening behavior of the stretching mode in $La_{1.2}Sr_{1.8}Mn_2O_7$ above T_C is somewhat similar to that observed in $La_{0.5}Ca_{0.5}MnO_3$ and $Bi_{0.18}Ca_{0.82}MnO_3$ near $T_{\rm CO}$. This observation is also consistent with the results of Fig. 4 (a), showing the existence of charge correlation effects in $La_{1.2}Sr_{1.8}Mn_2O_7$. In addition, the abrupt softening of $\omega_{\rm TO}$ below T_C should be understood in terms of the melting of the short range spatial correlation influenced by the spin ordering.

All our experimental findings suggest that there should be intimate coupling among charge, spin, and lattice degrees of freedom (through polaron) and that they interplays with each other in $La_{1.2}Sr_{1.8}Mn_2O_7$. Especially, short range spatial correlation effects of the charge, spin, and lattice degrees of freedom can be used to explain the T-dependence of $\sigma(\omega)$, such as the gap-like behaviors and increase of small polaron peak frequency in the mid-infrared region. [And, the dynamic fluctuations of those various degrees of freedom can be also important in a similar T window.]

In summary, optical conductivities in $La_{1.2}Sr_{1.8}Mn_2O_7$ indicate that the short range correlation of polarons exist above T_C, and that the sample remains as small polaron state even at 10 K. Subtle balance and competition among the spin, charge, and lattice degrees of freedom should be considered in understanding optical properties of the layered manganite.

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